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CR 151183

SC507.30AR

January 31, 1977

LUNAR SAMPLE ANALYSIS

ANNUAL REPORT NO. 5

For Period

February 1, 1976 thru January 31, 1977

General Order No. 507

Contract No. NAS9-11539

N77-18979

Unclass
16347

G3/91

CSCL 03B

(NASA-CR-151183) LUNAR SAMPLE ANALYSIS
Annual Report, 1 Feb. 1976 - 31 Jan. 1977
(Rockwell International Corp., Thousand
Oaks) 8 p HC A02/MF A01

Prepared for

National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Science and Applications Directorate
Houston, Texas 77058

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| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|-----------------------|--|
| 1. REPORT NUMBER | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) LUNAR SAMPLE ANALYSIS ANNUAL REPORT NO. 5 | | 5. TYPE OF REPORT & PERIOD COVERED Annual Report Feb. 1, 1976 thru Jan. 31, 1977 |
| | | 6. PERFORMING ORG. REPORT NUMBER SC507.30AR |
| 7. AUTHOR(s) R. M. Housley (Principal Investigator), R. W. Grant and E. H. Cirlin | | 8. CONTRACT OR GRANT NUMBER(s) NAS9-11539 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Rockwell International Corporation/Science Center 1049 Camino Dos Rios Thousand Oaks, California 91360 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS None |
| 11. CONTROLLING OFFICE NAME AND ADDRESS National Aeronautics and Space Administration Lyndon B. Johnson Space Center Houston, Texas 77058 | | 12. REPORT DATE January 31, 1977 |
| | | 13. NUMBER OF PAGES 8 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | | 15. SECURITY CLASS. (of this report) Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |
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| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) ESCA, Sputtering, Atomic Absorption, Lead, Volatile Metals, Surface Composition, Solar Wind, Regolith, Reduced Fe | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We report ESCA studies of the surface composition of lunar fines, the solar wind sputtering process, and the profile of reduced Fe in lunar samples. We also report atomic absorption studies of trace metal, especially lead, distribution in lunar fines samples. | | |

AN ESCA STUDY OF REDUCED Fe AND OTHER SURFACE CHEMICAL ALTERATION
PROFILES IN LUNAR FINES: R. M. Housley and R. W. Grant, Rockwell International
Science Center, Thousand Oaks, California 91360.

Previous ESCA studies have documented the existence of substantial quantities of reduced Fe in the surfaces of grains in lunar fines samples (1,2). They have also shown complex alterations in surface composition (3,4). In this report we present information on the profiles of reduced Fe and chemical alteration obtained by combining controlled sputtering with ESCA measurements.

Sputtering was done in the sample preparation chamber of the ESCA apparatus permitting spectra to be obtained after sputtering without exposing samples to air. During sputtering the system was always dynamically pumped and a pressure of 2×10^{-5} torr Ar with less than about 1% impurities maintained throughout the sputter. The sputtered region was larger than the area analyzed, with an average current density over the analyzed region of $6.2 \mu\text{a}/\text{cm}^2$. The Ar^+ energy was 1 keV and the sputtered surface was illuminated with thermal electrons from a hot filament to control charging.

The sputtering rate under these conditions was directly determined by masking a polished surface of S-17-3 and sputtering long enough to generate a step that could be measured with a mechanical stylus profilometer.

Prior to sputtering the lunar samples, we studied the sputtering behavior of a number of oxide and silicate minerals. Preferential sputtering, although observed, was generally modest. In no case was reduction of Fe^{++} in silicates by sputtering observed. Typical results comparing the composition of our synthetic glass standard S-17-3 after 90 minutes of sputtering with its bulk composition are shown in Table I.

The observed absence of gross chemical fractionation and Fe reduction is contrary to interpretations commonly given to several other experimental and theoretical studies, and therefore requires discussion. The work that apparently shows the most convincing evidence of direct sputter reduction of silicates is that of Yin *et al.* (5). However, their sputtering was done with a high pressure glow discharge, and gas composition during sputtering was not monitored. In such a system complex chemical reactions involving samples, electrodes, and supporting structures, can occur. This possibility and the frequent long time delay before reduction is observed (6,7) lead us to concur with the conclusion of Yin *et al.* (7) that their observed reduction is chemical rather than physical in nature. Hapke *et al.* (8) find chemical fractionation and an undetermined amount of Fe reduction in sputter deposited films. This does not conflict with our results. Kim and Winograd (9) have argued on the basis of experimental results and an empirical thermodynamic model that Fe_2O_3 would reduce to Fe_3O_4 and that FeO might reduce to metal on sputtering. They made no prediction for Fe^{++} in silicates. Pillinger *et al.* (10) have attempted to refine the thermodynamic model of sputtering and conclude that reduced Fe should build up to high concentration in the surface of lunar samples.

It appears to us that a logical extension of the thermodynamic model of sputtering would assume that during sputtering the samples behave in the same way as they do during thermal vaporization. This point of view and the thermodynamic data of Sato (11) lead to the conclusion that reduced Fe would

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not build up in the surface of lunar samples during sputtering in agreement with our observations.

Profiles of composition and reduced Fe obtained during sputtering of the same sample of 15301,85 which we previously studied (2,4) are shown in Table I. Compositions were determined by the procedure described previously (4). The reduced Fe ratios were determined from the peak heights in the Fe 2p region and may be in error by approximately a factor of two because of assumptions made concerning the line shapes.

Table I. Composition profiles in S-17-3 and 15301 in atomic percent.

| Time Sec | Depth Å | $\frac{Fe^0}{Fe}$ | K | Si | Al | Mg | Fe | Ca | Ti | O | Remarks |
|-------------|------------|-------------------|------|-------|------|------|------|------|------|-------|--------------------------|
| — | — | 0.0 | — | 15.34 | 3.60 | 4.29 | 8.33 | 4.25 | 3.35 | 60.14 | S-17-3 bulk |
| 5400 | 50 | 0.0 | — | 13.6 | 3.4 | 4.5 | 9.6 | 4.5 | 4.6 | 59.9 | S-17-3 sputtered |
| — | — | — | — | 16.2 | 6.5 | 6.8 | 4.2 | 4.0 | 0.3 | 62.0 | 15301 bulk calculated |
| 0 | 0 | 0.13 | 0.75 | 20.5 | 5.3 | 3.6 | 5.3 | 3.9 | — | 61.4 | 15301 run Dec. 1974 |
| 0 | 0 | 0.06 | 1.07 | 19.2 | 5.6 | 3.9 | 5.8 | 4.8 | — | 60.8 | 15301 run Dec. 1976 |
| 100 | 1 | 0.16 | .58 | | | | | | | | " |
| 400 | 4 | 0.25 | .45 | 19.6 | 6.2 | 3.8 | 5.7 | 3.9 | — | 60.8 | " |
| 1000 | 9 | 0.24 | .31 | 18.5 | 7.0 | 3.9 | 5.4 | 4.0 | 0.5 | 60.7 | " |
| 2000 | 18 | 0.23 | .19 | | | | | | | | " |
| 3000 | 27 | 0.22 | — | 16.9 | 7.7 | 4.6 | 5.0 | 5.0 | 0.6 | 60.2 | " |
| 4000 | 37 | 0.22 | — | | | | | | | | " |
| 6000 | 55 | 0.14 | — | | | | | | | | " |
| 8000 | 73 | 0.16 | — | 14.7 | 8.7 | 5.7 | 4.9 | 5.7 | 0.7 | 59.5 | " |
| 10000 | 92 | 0.16 | — | | | | | | | | " |
| 14000 | 128 | 0.12 | — | | | | | | | | " |
| 18000 | 165 | 0.13 | — | 13.9 | 8.3 | 5.9 | 4.6 | 6.5 | 1.3 | 59.4 | " |

It can be seen from the data in Table I that the reduced Fe fraction in the surface of 15301 fines only decreased by about a factor of two after 2 years exposure to air. More surprisingly, after only 4Å of sputtering, it increased to about twice the initial value. At greater sputtering depths it decreased very slowly suggesting that probably significant reduced Fe exists considerably deeper in the samples than the 165Å so far sampled.

If a large fraction of the reduced Fe is compensated by H as we have suggested, the profile of reduced Fe probably simply reflects the diffusion profile of solar wind H into the samples. In this regard recent work (12) suggests that hard ultraviolet radiation may free H from trapping sites and dramatically enhance diffusion rates.



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The K seen in 15301 is probably on the exterior surfaces of green glass ball fragments. Our results suggest that these fragments have a coating about 20Å thick which is very rich in K.

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AN ATOMIC ABSORPTION STUDY OF VOLATILE TRACE METALS IN LUNAR SAMPLES,
E. H. Cirlin and R. M. Housley, Rockwell International Science Center, Thousand
Oaks, California 91360.

Since the first analyses of lunar samples were reported, it has been apparent that many volatile trace metals are enriched in lunar fine regolith material by factors of typically 3 to 10 with respect to the parent rocks. This might be due to the addition of extralunar, principally meteoritic material to the regolith. It might be due to outgassing associated with lunar igneous activity or hot impact ejecta blankets. Since meteorites largely or completely vaporize on impact, volatile metals from either source would be expected to be on or near the surface of grains in the regolith.

The feasibility of outgassing models might be tested by analyzing for surface deposits on the cracks and pores in igneous rocks and impact breccias.

The source and chemical evolution of Pb in the regolith is of special importance since this element is used for geochronological studies of regolith evolution (1,2), and it has been suggested that significant Pb loss by volatilization accompanies agglutinate glass formation (1,2).

We are in the process of developing atomic absorption methods for the analysis of trace volatile metals in lunar and meteoritic materials using direct atomization of solid samples. Since no chemical treatments are required, analyses can be performed quickly and simply. The sensitivity is sufficiently high, for the elements of principal geochemical interest, that analyses can be performed on submilligram samples, making it easy to study particle separates or even individual submillimeter grains. The thermal release profiles can be used to obtain additional information on the chemical sites of the elements in the samples.

We are using a Varian AA-6 atomic absorption spectrophotometer with a Model 63 carbon rod atomizer and a BC-6 background corrector unit. All data have been obtained by using the slowest ramp heating mode during the atomization part of the heating cycle, and with the carbon sample container and sample bathed in a flowing H_2-N_2 gas mixture.

We have studied a number of natural and synthetic samples and at this time can present and discuss survey data on Pb in a limited set of lunar samples. Representative Pb thermal release profiles are shown in Fig. 1.

We have used a dilute solution of $Pb(NO_3)_2$ as a reference sample. It is known to decompose to PbO before atomization. As can be seen in Fig. 1a, it yields a very sharp thermal release peak. Surface Pb on finely crushed SiO_2 which had been exposed to a dilute solution of $Pb(NO_3)_2$ gave a nearly identical peak. So did a sample which was crushed in a mortar which had not been acid washed, and a sample which was washed in glassware that had not been adequately cleaned. Laboratory dust gave a similar but exceptionally strong peak at the same position. Finally, colloidal PbS prepared by reacting a dilute solution of $Pb(NO_3)_2$ with Na_2S gave an indistinguishable peak.

Thus, natural surface Pb, in either the PbO or PbS form as well as all sources of contamination we have encountered to date, can contribute to this first "surface Pb" peak. The rest of the release profile is very insensitive to these sources of contamination.



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Figure 1b shows typical data obtained on a sample of Precambrian Montello, Wisconsin granite. The high temperature peak is not due to Pb but is molecular background caused by the vaporization of SiO from the silicates. As seen in Fig. 1c, it is completely eliminated in the background corrected mode. Silicate background was similarly eliminated in the data shown in Figs. 1d, 1e and 1f.

The data in Figs. 1b and 1c strongly suggest that except for surface Pb of undetermined significance the bulk of the Pb in Montello granite is in a single well defined mineral phase.

The data on crystalline rock 75035 shown in Fig. 1e show no surface Pb and only a weak broad peak at intermediate temperatures. They thus provide no evidence for Pb outgassing associated with normal lunar igneous activity.

The data on the orange glass fines 74220 shown in Fig. 1f show a strong surface Pb peak as expected, which however tails to high temperatures indicating that some Pb comes from the interior of grains.

The data in Fig. 1d on $<45\ \mu\text{m}$ fines separated under our normal laboratory conditions show a strong surface Pb peak and two substantial higher temperature Pb peaks. The surface peak on this sample is at least partly due to contamination.

We have normally kept a fraction of all our fines samples unprocessed in the original plastic bottles for trace analysis. We have looked at several samples each, from our original fractions of 10084, 15031, 67701, and 75081. All show some surface Pb and all but 67701, which does not show a well defined high temperature peak, show the other two peaks.

The original samples of 67701, which has a short surface exposure age and low agglutinate content, and 10084, which has a long exposure age and high agglutinate content, both have roughly 25% of their observed Pb in the surface peak. These data provide no support for a correlation between surface Pb and micrometeorite bombardment, surface exposure, or agglutinate content.

Two recent sieve fraction results, though in need of further confirmation with more samples, seem especially interesting. 1) The $>150\ \mu\text{m}$ fraction of 10084 fines although containing abundant regolith breccia fragments shows no surface Pb peak. 2) A $<10\ \mu\text{m}$ fraction of 10084 fines prepared by dry sieving under clean conditions shows total Pb and surface Pb fraction no higher than the bulk $<1\ \text{mm}$ fines.

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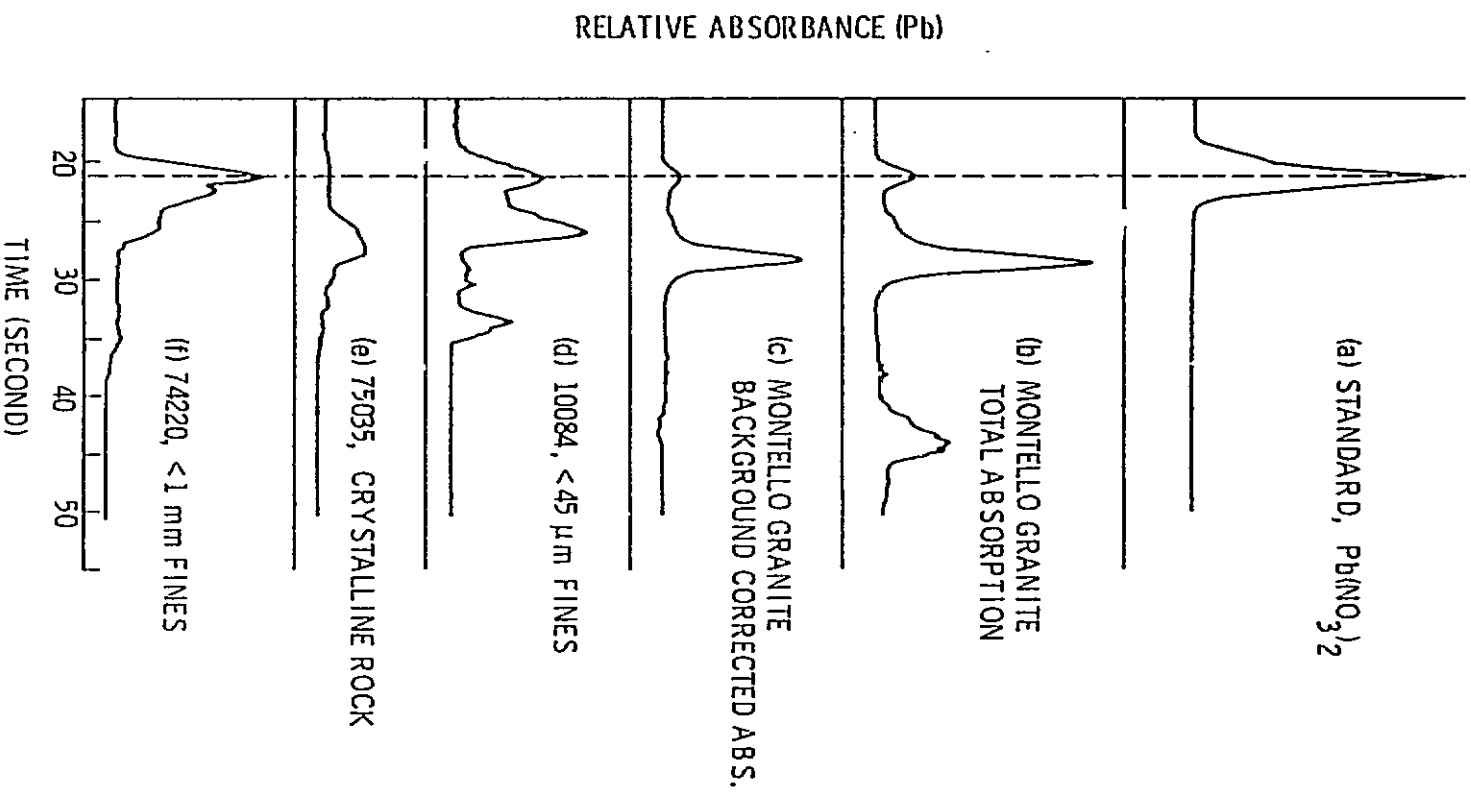


Figure 1. Thermal Pb release profiles for representative terrestrial and lunar samples obtained with ramp heating. The absorbance is directly proportional to the number of ground state atoms in the light path at any time.